Composition effects on the early-stage oxidation kinetics of (001) Cu-Au alloys

Scientific Achievement

The *in situ* TEM studies indicate that oxidation of Cu-Au alloys starts with nucleation of isolated oxide islands that quickly reach a saturation number density. Quantitative measurements indicate that the saturation density depends on the oxidation temperature and the Au concentration in the alloys, *i.e*., a higher oxidation temperature results in a smaller number density of oxide nuclei, and a higher Au mole fraction gives rise to a larger number density of nuclei. The saturation island density follows an Arrhenius dependence on oxidation temperature. The activation energy for the nucleation of oxide islands are determined by measuring the island density at different oxidation temperatures. The analysis indicates that Au enhances the nucleation of oxide islands.

Growth of the oxide islands was observed in real time during the oxidation. A linear growth behavior of the oxide islands was noted from the quantitative measurements. The rate constants for the growth of oxide islands were determined during oxidation of the alloys with different Au mole fraction, and it is noted that the alloys with a larger Au mole fraction have a smaller growth rate. Our results indicates that Au suppresses growth of oxide islands.

Significance

Our results indicate that alloying Cu with Au decreases the passivation properties of Cu, and we expect the present results will impact future alloy design for increased oxidation resistance. One common application of alloying is in the development of materials with enhanced oxidation resistance, which results from the formation of a continuous oxide layer covering the metal surface. Much progress has been made in understanding later-stage oxidation, as formulated by Wagner and modified Wagner-type theories that account for short-circuit diffusion paths within the oxide layer. The passivation behavior of metals is strongly influenced by the microstructures of the oxide film that forms. For example, a high density of short circuit diffusion paths within the oxide layer often leads to poor oxidation-resistance. The morphology of the oxide film can be strongly influenced by the oxide nucleation and early-stage growth behavior. However, detailed information regarding the nucleation and growth of oxide in the early-stage oxidation is still very limited, especially in the case of alloys. Our investigation indicates that Alloying Cu with Au enhances nucleation of oxide islands, but suppresses the island growth rate and causes a large number of interfaces and defects in the oxide film due to the accumulation of rejected Au atoms around the oxide islands which prevents the perfect coalescence of the islands.

Performers

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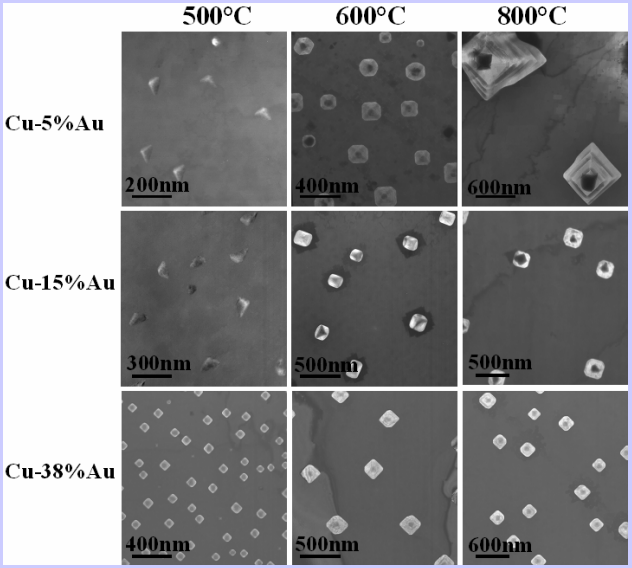
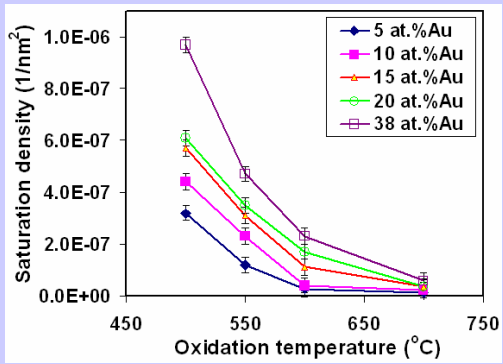
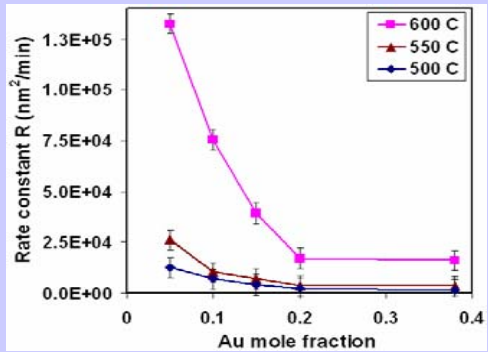
Effect of alloying on nucleation and growth of oxide islands



TEM micrographs of Cu_2O island formed during Cu-Au oxidation at different temperature in $pO_2=5\times10^{-4}$ Torr.



(a)



(b)

Increasing Au mole fraction in the alloy leads to an increase in the island saturated number density (a), and a decrease in the growth rate of oxide islands (b).

- **Au increases the nucleation of oxide islands, but suppresses the island growth rate.**
- **Alloying Cu with Au decreases the passivation properties of Cu due to the accumulation of rejected Au atoms around the oxide islands which prevents the perfect coalescence of the islands.**

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